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## An Evaluation of Permanence Using Wet and Dry Accelerated Aging

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An Evaluation of Permanence Using  
Wet and Dry Accelerated Aging

by

Patricia M. Kern

A Thesis submitted  
in partial fulfillment of  
the course requirements for  
The Bachelor of Science Degree

Western Michigan University  
Kalamazoo, Michigan  
August, 1978

## ABSTRACT

Evaluation of a series of paper samples aged using wet and dry accelerated methods showed that there is a definite difference between the two methods.

Electrometric pH and folding endurance provided the best indication of the deterioration of the paper properties upon aging.

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When George Orwell penned his forbidding vision of life in nineteen-eighty four, he didn't foresee in that catalog of frightening predictions the ironic fact that the first copies of his work, published in 1949, are not likely to last until 1984.(44) Many other books only 25-50 years old are already so weakened and deteriorated that their future usefulness is also questionable. (34)

The untimely deterioration of books is not a new problem. Paper was introduced to Europe in the 11th century. For many years parchment users scorned it since it didn't have the permanence of parchment. The Emperor Frederick II required that all documents pertaining to the constitutions of the Two Sicilies be written on parchment so 'that they may bear testimony to future generations and not risk destruction through age.' (37) However, in spite of imperial discouragement, the manufacture of paper grew to the point where it could support the publishing industry when printing was introduced in the latter half of the 15th century.

In the 15th century and earlier, there is no evidence of large losses of paper records due to causes that would not have been equally harmful to parchment. The combination of sound, high-quality raw materials, mild or absent chemical treatment and the use of clean, hard water added up to produce 15th century papers that were just about as good as parchment.

By 1500, however, papermaking had become the dominant industry and only a few nostalgics insisted on the more costly parchment. Once freed from competition with parchment, papermakers faced only intra-industry

competition and quality began to suffer. Top quality raw materials always seemed to be scarce and manufacturers began to adopt "improvements" that allowed them to meet the ever increasing demands for paper by utilizing lower quality raw materials.

The results of these "improvements" were slow in coming, but the effects were cumulative. The severity of the chemical and mechanical treatments experienced by papers of each century since the 15th has increased dramatically. (37) All of the factors leading to increased degradation are not known, but among the most important is the effect of acidity on paper properties. The late W.J. Barrow made several important studies dealing with this topic. (15,23,25)

Barrow, a document restorer of Richmond, Virginia, began his work during the Depression. As he observed restoration techniques, he became increasingly aware of the part played by acidity in the embrittlement of paper. His own observations from 1939 showed that deteriorated documents were invariably high in acid content compared to new sheets of the same type.

In 1957 the Council of Library Resources and the Virginia State Library agreed that Barrow should be contracted to find out what was happening to the book papers of the early 20th century. In the study, Barrow tested 500 non-fiction US books, 10 for each year in the period 1900-1949 for folding endurance, tearing resistance and acidity/alkalinity.

The results showed that paper from the average non-fiction US book of 1900-1910 had lost 96% of its original strength by 1957. Papers of the period 1940-1949 had already lost 64% of their strength. Based

on this sample, most of the books printed in the US during the period 1900-1949 could not expect to be usable in the 21st century. In 1959 Barrow noted that the deterioration among the tested papers was proportional to their acidity. (15)

Encouraged by the success of his first study, Barrow went on to study writing papers of 1425-1900 and book papers of 1800-1899.

The study of writing papers 1435-1900 showed that papers of the second half of the 17th century were 16 times as acidic as those of the first half. Their strength as measured by folding endurance had dropped  $\frac{2}{3}$  from 850 to 250 folds.

At the time of his death in 1967, Barrow was planning studies on the papers of the 18th, 17th and 16th centuries. The examinations of these papers were later completed under the guidance of Dr. Robert N. Dupuis at the Barrow Laboratory. Referring to these studies, the history of the degradation of paper can be followed.

In 1774 Karl Wilhelm Scheele discovered chlorine. Chlorine bleach was soon commonly used to effectively whiten and decolor dyed or inferior cloths formerly unacceptable for the manufacture of book paper. Many early bleaching attempts ended in serious embrittlement of the paper. In 1829 Scottish lecturer and writer John Murray spoke of bleaching as the chief source of degradation of paper of that period. Chlorine is a strong oxidizing agent and trace amounts of it can unite with moisture to form hypochlorous acid. Sutermeister noted that such common practices as over-bleaching to too high brightness, use of high temperatures to hasten the bleaching reaction and the utilization of anti-chlor to



stop the chlorination process all contributed to the deterioration of paper properties. (37) Papermakers have since learned how best to control bleaching chemicals.

By the middle of the 17th century it was already standard practice to size books and writing papers in order to avoid penetration and feathering of ink. Until the 19th century, animal glue, (a crude gelatine), was the principal material used for this purpose. Alum (potassium aluminum sulphate) was introduced in the mid 17th century as a means of hardening the gelatine and preventing it from putrifying in the sizing tub. Once in the paper mill, alum became what S.D. Warren paper chemist Dr. Edwin Sutermeister later called 'one of the most generally used curealls in the mill.' (37) To the librarian and the archivist, it is significant because of its injurious acidity and the degrading effect it has on paper strength.

The history of modern paper is heavily influenced by the use of rosin-alum size. In 1807 Moritz Friedrich Illig published a pamphlet describing a method of cheaply and easily engine sizing paper. (1)

Illig's procedure consisted of adding rosin boiled with soda to make sodium resinate to the beater. After mixing, alum was added.

The rosin precipitates onto the fibers as aluminum resinate. The finished paper has enough water repellency to allow inks to be used without feathering. Rosin-alum sizing makes sizing a part of stock preparation rather than a separate operation. It uses cheap, stable ingredients and has been used to give a variety of effects such as enhanced rattle, reduced foaming, improved filler retention and better handling

of sticky stock.

Unfortunately, the rosin-alum sizing system works most effectively at pH 4.5-5.0 and encourages excess acidity in the papermaking operation since it leaves free sulfuric acid as a by product of the rosin-alum soap reaction. Barrow felt that the introduction of rosin-alum size contributed more to the deterioration problems in paper than any other development of the 19th century.

The invention of papermaker's alum exacerbated the problem. The product of reacting bauxite ore with sulfuric acid was highly touted as "concentrated alum" since it gave the papermaker twice as much aluminum ion for the money. Unfortunately, papermakers' alum often contains residual sulfuric acid from its manufacture as well.

Barrow's study of book papers 1800-1899 yielded many interesting results. The papers from 1800-1849 were all rag. Those from 1800-1809 were the weakest, indicating that the chlorination problems seen during this period may be contributing to the deterioration of the paper. From 1810 to 1849 a steady increase in strength is seen, indicating adjustments to the demands of the Industrial Revolution on the art of papermaking as well as the effects of decreasing age. Still, even at its highest point, the strength of the papers from 1830-1849 (as tested in 1963-1965) is only equal to that of new newsprint and has only 4% of the median strength of the writing papers of 1601-1650 mentioned previously.

1850 marked the beginning of a downward trend in strength. From a median of 35 folds (1840-1849), the strength dropped to less than 2 folds (1890-1899), the all-time low for book papers.

Since the swift decline in paper strength after 1850 coincided with

the introduction of wood pulp as a rag substitute, popular belief has made all-rag paper a symbol of permanence. Barrow disagreed with this idea since the decline in strength from 1840-1849 was also accompanied by a 6-fold increase in acidity. This increase in acidity is to be expected since the amount of alum usage in paper increased from 10% in 1840-1849 to 87-97% in 1890-1899. At that point in time virtually every piece of paper made contained some amount of rosin-alum size.

Even if rosin-alum size had been accepted as the primary source of paper deterioration, the process was so cheap and the possible consequences of its use so remote, that mere predictions of future problems had little or no effect on its use.

The rudimentary chemical knowledge of the 18th and 19th centuries allowed the art of papermaking to far outrun its science. Systematic studies of paper began in the 1880's at the Royal Material Testing Bureau in Charlottenberg. Little attention was paid to the role of pH in predicting the permanence of paper until the tremendous advances in paper science that occurred in the early 20th century were able to make the necessary technology available. (37) By the mid-1920's paper science had come far enough to make a technical discussion of permanence profitable.

No sufficiently sensitive method of determining the pH of paper was available at that time, so the investigators were forced to develop their own. In 1925 Köhler and Hall of the Swedish Government Testing Bureau published a method of determining the acidity of paper using an improved titration method. The method consisted of extracting fluffed paper up to 7 times in hot water and measuring the cc's of standard dilute alkali

required to neutralize it using phenolphthalein as an indicator. This procedure was sensitive enough to differentiate among papers of different sizing levels. Köhler and Hall concluded that the papers with the highest rosin contents were the most acidic. (2) They checked their results by aging the samples at 100 C for 125 hours. The losses in folding endurance were proportional to the amounts of size and the acidity ratings of each sample. In 1928 these results were confirmed by W.H. Hoffman of the Northwest Paper Company. Hoffman concluded that the hot water extract of a permanent paper should be no less than 4.5 and preferably higher than 4.7 to avoid premature degradation. (3)

The US Bureau of Standards adopted the Köhler-Hall method for measuring total acidity and used it until the invention of the pH meter rendered it obsolete. It was found that many alkaline papers yield poor results by this method because of interference from such additives as calcium carbonate and casein. The total acidity as measured by the Köhler-Hall method is not necessarily even closely related to the pH of the water extract. (32)

After the development of the Köhler-Hall technique, appreciation of the fact that more alkaline pH values were needed for permanent papers began to grow.

According to the current literature, the two general methods of preparing water extracts of paper for pH measurement are hot and cold extraction. (32,34) Below pH 7 the pH of a hot water extraction may be one or more units below that of a cold water extraction of the same sample. This difference is attributed to the fact that alum hydrolyzes to a greater extent in hot water.

Although the hot water extract is considered to be more indicative of a paper's probable permanence, there is not complete agreement as to which of the methods is actually more truthful or accurate. The cold water extraction gives more consistent results when the rate of aging is judged by measuring the rate of decrease of folding endurance. At least one gram of paper is needed for each extraction, hot or cold. The paper is extracted using a standard procedure and the pH of the water solution is determined using indicators or a pH meter. The paper samples must be handled carefully to avoid contamination with skin oils or alkaline or acidic vapors. All glassware must be acid cleaned with 1:1 nitric acid after each use. The process is time-consuming and destroys the paper sample.

Dr. Robert Mareck, (45) the librarian of WMU's Institute of Cistercian Studies, states that one of his primary concerns in evaluating valuable old manuscripts and books is determining the pH of the sheets without harming them. Restorative treatment is indicated if the pH is too low. He is also concerned with the initial pH of the various papers and boards used to mount old works. Acid migration from the substrate into the old paper has exacerbated deterioration in the past.

When the paper sample is too valuable to cut up into 1 gram pieces for testing, other methods of determining the pH are available. Electrometric and color indicator methods are discussed by Browning(32), King, Pelikan and Falconer(35) and Buck(35).

In the electrometric method, a glass flat-head electrode and a reference electrode are applied to the moistened surface of the paper sample. Use of a potassium chloride solution to moisten the sheet gives

lower, more reproducible results. The 0.1 M salt solution apparently extracts the acid more thoroughly; possibly by an ion exchange mechanism. (32) The method is quick, non-destructive and useful for estimating the acidity of paper, which makes it desirable for examining books and documents of archival value. The results may vary considerably from those of the cold water extract, though close correspondence is often seen. pH of the paper surface can be compared to that of the water extract only if the sheet is assumed to be homogenous.

pH can also be estimated by spotting the paper surface with an appropriate acid-base indicator solution. The indicators most commonly used for this purpose are Bromocresol Green, Bromocresol Purple and Bromophenol Blue. (36) Methyl Red, Chlorophenol Red, Bromthymol Blue and Cresol Red have also been tried. (35) The indicator solutions were applied with the tip of a glass rod and examined for color changes within 3 minutes. The Methyl Red gave faint, difficult-to-read results. All of the indicator spots changed color on drying except those of the Chlorophenol red, but rewetting restored the color in every case.

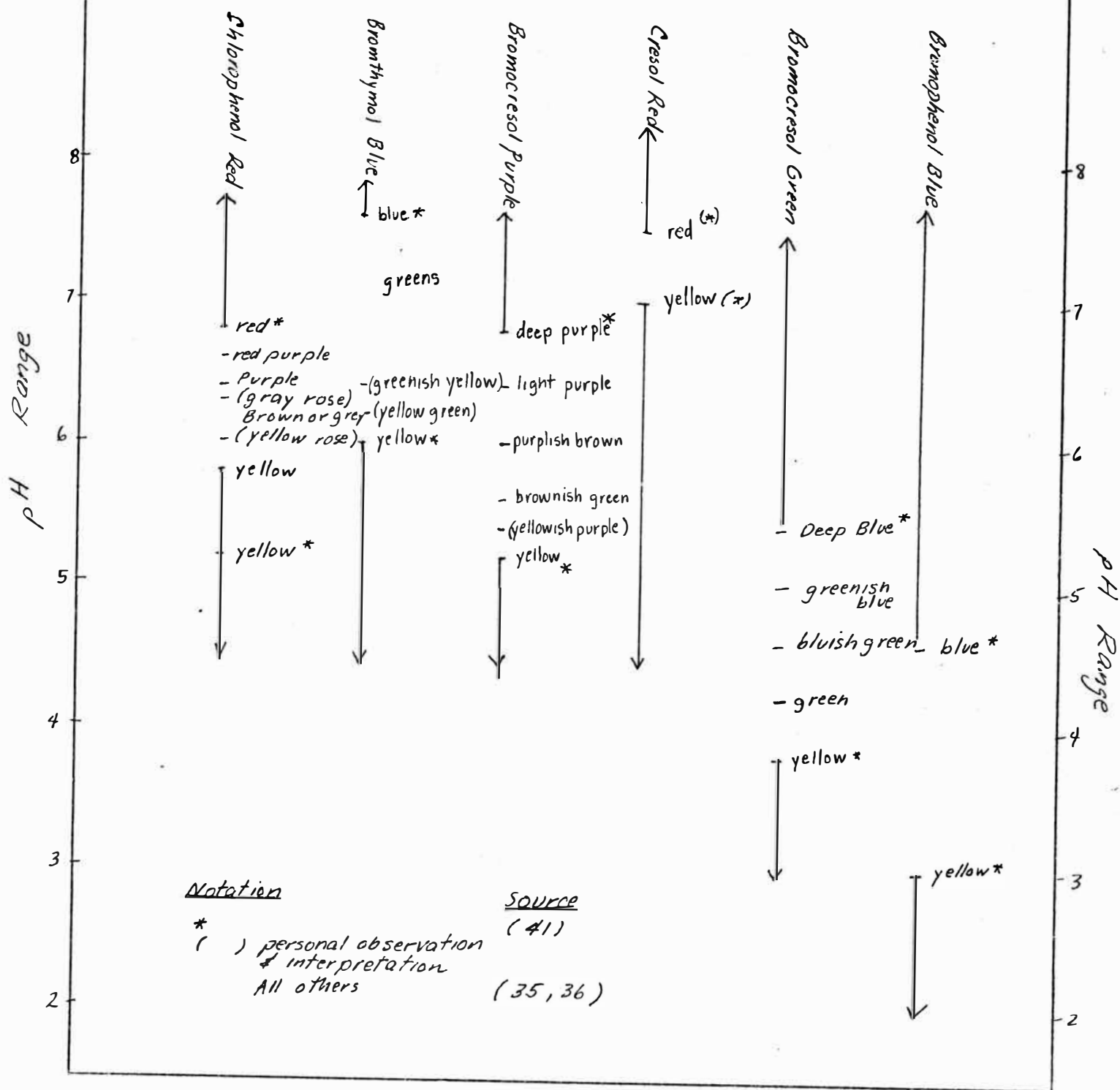
A Universal pH indicator solution has also been used. (36)

Indicator methods yield pH values that are in approximate agreement with those of water extraction procedures. The method is not as reliable in papers that yield unbuffered extracts, because of the buffering action of the indicator.

Surface pH measuring methods may not necessarily match water extract values, but they are quite useful in terms of ranking papers according to relative acidity.

Quite a bit of controversy over the "best" method of pH measurement centers around the interpretation of the term "pH". The pH of

# Indicators



COLOR CHART for DETERMINING pH by  
INDICATOR METHOD

paper is a rather nebulous concept since a heterogeneous dispersion of fibers is hardly the same as the aqueous solution for which pH is defined. It is necessary to state clearly whether hydrogen ion concentration or total acidity or some other quantity is being called pH.

In 1931 R.H. Rasch of the Brown Company used heat aging to test paper stability and found that when acidity was controlled at pH 5.0 a highly stable sheet resulted. (4)

The value of such an accelerated aging test was challenged on the grounds that it had not been proven by natural aging. In 1933 Rasch and Schribner (5) and in 1939 Schribner (6) alone examined 4 and 8 year old samples of the 1929 test papers and confirmed the original results. In 1955, Dr. W.K. Wilson of the US National Bureau of Standards reported on the papers at 22 and 26 years and concluded that the effects of natural and heat aging showed a fair correlation. Most commonly, natural and accelerated aging have been compared by empirical correlations based on the previously mentioned study. A number of investigators agree that 72 hours at 100 C is equal to 20-30 years of natural aging. (11,23)

The most important factor influencing the accelerated aging process is the moisture content of the sheet during aging. Most accelerated aging methods do not utilize humidity control and the water content of the sheet is far below normal during aging. Air at 20 C and 50% relative humidity(R.H.) will have a R.H. of only 1.15% at 100 C and the sheet moisture will be low too.

If the moisture content of the sheet has anything at all to do with the reactions going on during aging, the results of "dry" aging would be invalid. Browning (8) believes that aging should be done at a constant



sheet moisture and at a series of different temperatures to allow calculations related to the kinetic study of paper permanence to be made. Dry accelerated aging tests such as Tappi T453, made using only one temperature are inaccurate for ranking samples for potential permanence. (33)

Drying out of the sheet at high temperatures can be avoided by maintaining a high relative humidity in the oven, or by sealing the samples in closed tubes. A constant R.H. does not insure constant moisture conditions in the sheet because of the sorption isotherms that exist at different temperatures. Since the aging properties are related to the actual moisture content of the sheet, it would seem advisable to adjust the R.H. to make sure that the same amount of moisture is present in the sheet at different temperatures. At 50% R.H. or less, temperatures of up to 120 C can be used without major difficulties. If possible, the sheet moisture should be maintained at the level it had under standard conditions.

Aging in closed containers will maintain a reasonably constant moisture content if the amount of paper is large compared to the volume of the container. Unfortunately, neither the R.H. nor the sheet moisture at a specific temperature can be known. In addition, the oxygen content in the container may change, and volatile decomposition gases may be trapped within as well.

In 1960 G.E. Gray (33) listed a number of chemical mechanisms that may contribute to the deterioration of paper during aging. These include atmospheric oxygen, residual calcium chloride and alum combining to yield aluminum chloride which could release hydrochloric acid, sulfur

dioxide and rosin sizing. Whatever its origin, acidity seems to be one of the main causes of deterioration.

Paper also changes chemically and physically with time as a result of reduction of bonded area in the sheet and structural changes in the cellulose itself. The stability of the cellulose fiber can be measured by copper number, viscosity and solubility in strong alkali solution.(11) However, none of these tests can give much more than a general indication of quality. They can, for example, detect extensive degradation.

Testing methods preferred by various researchers depend on the end use of the sheet and include the following; folding endurance(11,13, 15,20,30,32), tensile strength(11,15,30,32), pH(11,15,20,36), brightness or color loss(20,32) and tearing resistance(20,32). Zerospan tensile and specific absorption are also mentioned.(30)

Folding endurance is the most commonly used because it decreases rapidly during accelerated aging. While it is considered to be the most significant test for paper permanence, it is also intrinsically variable and controversial. Folding endurance is a function of basis weight, thickness, moisture content of the sheet and the amount of load applied during the test to name just a few variables. The influence of tensile strength grows as the aging sequence progresses. The sensitivity of the test can be decreased by normalization. When the load is decreased in the same ratio as the tensile strength decreases on aging, a more linear relationship is observed. (31)

Throughout the literature, a trend toward increasingly realistic evaluation of paper permanence is seen. Questions related to the de-

gree of permanence are being voiced by many people from librarians to paper scientists.

### Experimental Procedure

#### Sample Manufacture and Preparation

On April 4, 1978, the samples for the project were made in the Western Michigan University Pilot Plant. A 50:50 blend of bleached hardwood and softwood kraft was refined to a Canadian Standard Freeness of 500 ml. The stock was run at 89fpm to give an approximate air dry basis weight of 44#/(25x38x500)ream. Various sizes and sizing levels were used to insure a definite difference in reaction to artificial aging. Two unsized blanks were also included; Sample 1 at high pH and Sample 10 at low pH. Since the choice of pH affects the performance of the rosin-alum and Aquapel-Kymene sizing systems, high and low pH samples for each were also included.

A summary of the 10 samples appears below:

Sample No.	Description	pH (approximate)
1	Unsize blank	6.2
2.	1/2%rosin;1/2%alum	6.2
3.	1/2%rosin;1/2%alum	5.5
4.	1%rosin;2%alum	4.3
5.	2%rosin;4%alum	4.2
6.	.1%Aquapel;.2%Kymene	4.2-5.4
7.	.1%Aquapel;.2%Kymene	7.3
8.	.2%Aquapel;.2%Kymene	7.3
9.	.4%Aquapel;.2%Kymene	7.3
10.	Unsize Blank	4.0

The finished samples were slabbed off of the roll, trimmed to a manageable size and then cut into the samples necessary for testing.

In order to eliminate errors due to basis weight and formation

differences, the sheets of each sample were shuffled and arranged in three groups (one each for fold, tensile and pH). Each group was cut into samples of the appropriate dimensions. These were shuffled again, then separated as randomly as possible into sets for aging (25 samples/set for fold, 10 for tensile, 15 for pH). Each set was stapled together and labeled. The samples were suspended in the ovens by a paperclip and string arrangement.

#### Aging Equipment

Two ovens, an Aminco forced draft oven and an Aminco 3-B Climate Lab were used to age the samples. Both were temperature controlled by bimetallic thermostats.

The Climate Lab was also equipped to control the relative humidity. After cleaning and minor adjustments had been completed, the Climate Lab was induced to operate in a stable manner. A 15 gallon carboy with a bottom spigot was used as a gravity feeding water source. Water fed from the carboy to the Climate Lab's interior reservoir through a section of plastic tubing. The drain spigot was connected to another section of tubing, which spilled into a floor drain. Care was required to maintain constant drainage while the oven was operating. If the drain hose was disturbed so that an air lock formed, the wet bulb reservoir would dry out and the recorder could no longer record the situation in the oven.

The wet and dry bulb temperature recorder on the Climate Lab was not designed for temperatures over 160 F, so the filled system dry bulb element was removed at the start of the aging cycle (176 F) and replaced by a 0-300 F thermometer suspended from an interior rack. This thermo-

meter could be observed without opening the inner (glass) door of the Climate Lab. The wet bulb temperature for the first aging cycle was only 140-145 F, so it was left in place until the second aging cycle was started.

The Climate Lab's manufacturer stated that either pen on the recorder could be offset up to 30 F, but that temperatures in excess of 190 F would over-range the recorder.

#### Aging Sequences

Two aging cycles were done in each oven.

80 C and 120 C were chosen as the temperatures for aging.

The moisture in the forced draft oven was assumed to be zero (dry). The moisture of paper at various water temperatures of the Climate Lab was evaluated. At 80 C a water temperature of 160 F gave an average sheet moisture of 3.1% on dry weight. This is considerably lower than the average moisture of the conditioned sheets(6.5%). However, 160 F gave the highest paper moisture for the dry bulb temperature, so it was used.

Samples were aged for 3,6,12 and 20 days.

#### Testing

Before the aging cycles were started, the basis weight and moisture content of the sample paper conditioned in the humidity room were determined according to normal procedures.

After the aging was completed, each sample was run through a series of tests. Tensile strength was determined by using an Instron Tensile tester set with a 4 inch jaw separation, pulling at 2 cm/minute.

Once the average tensile strength was known, a ratio was made between the tensile strength of the blank and that of the aged sample in question.

This ratio determined the amount of loading applied to the MIT fold tester in order to get folding endurance. Because of time limitations, 15 folds per sample were done for the majority of the samples. The remainder had 25 folds done on each.

pH was determined by using a series of indicator solutions recommended in the literature. (35,36) Bromocresol Green, Bromocresol Purple, Bromophenol Blue, Bromthymol Blue, Chlorophenol Red and Cresol Red were prepared as 0.04% aqueous alkaline solutions. The pH of each was adjusted to the center of its transition range. (41)

Three pieces of each sample were used in each test. Approximately 1/10 ml of each indicator was applied to the surface of the paper with an eyedropper, then spread out into a circle about 1 cm in diameter. After a few minutes the colors were observed and rated with the help of a chart derived from the literature. (See page 10)

A Möller combination pH electrode was also used to gather data. Pieces of each sample were folded into small sections and soaked for 5 minutes in Petri dishes containing 25 ml of water. The electrode was standardized using the appropriate buffer solution and then used to measure the pH of the soaked sample sections. The soaking period was required to wet out the paper due to the presence of the sizing material. Gloves and tweezers were used throughout the procedure to avoid contaminating the samples.

## Results

### Basis Weight

The values for O.D. basis weight varied from 40.29# to 43.00#.

The mean was 41.84# and the standard deviation was .93#. The air dry basis weight varied from 45.72 to 43.12#. The mean was 44.76# and the standard deviation was .94#.

#### Moisture

The moisture of the conditioned sheets ranged from 5.7 to 7.05% based on dry weight of the paper. The average was 6.52, the standard deviation .44%.

#### Folding Endurance

As expected, the fold proved to be a sensitive indicator of strength changes on aging. (See graphs, pages 19 and 20) A decrease in folding endurance with increasing alum and rosin concentration was noted. Higher than normal levels of Aquapel and Kymene, and use of this system at a low pH also resulted in losses in folding endurance. The low pH blank had poor strength after aging also. The wet aged samples were seen to lose more strength than the dry ones, especially at 120 C.

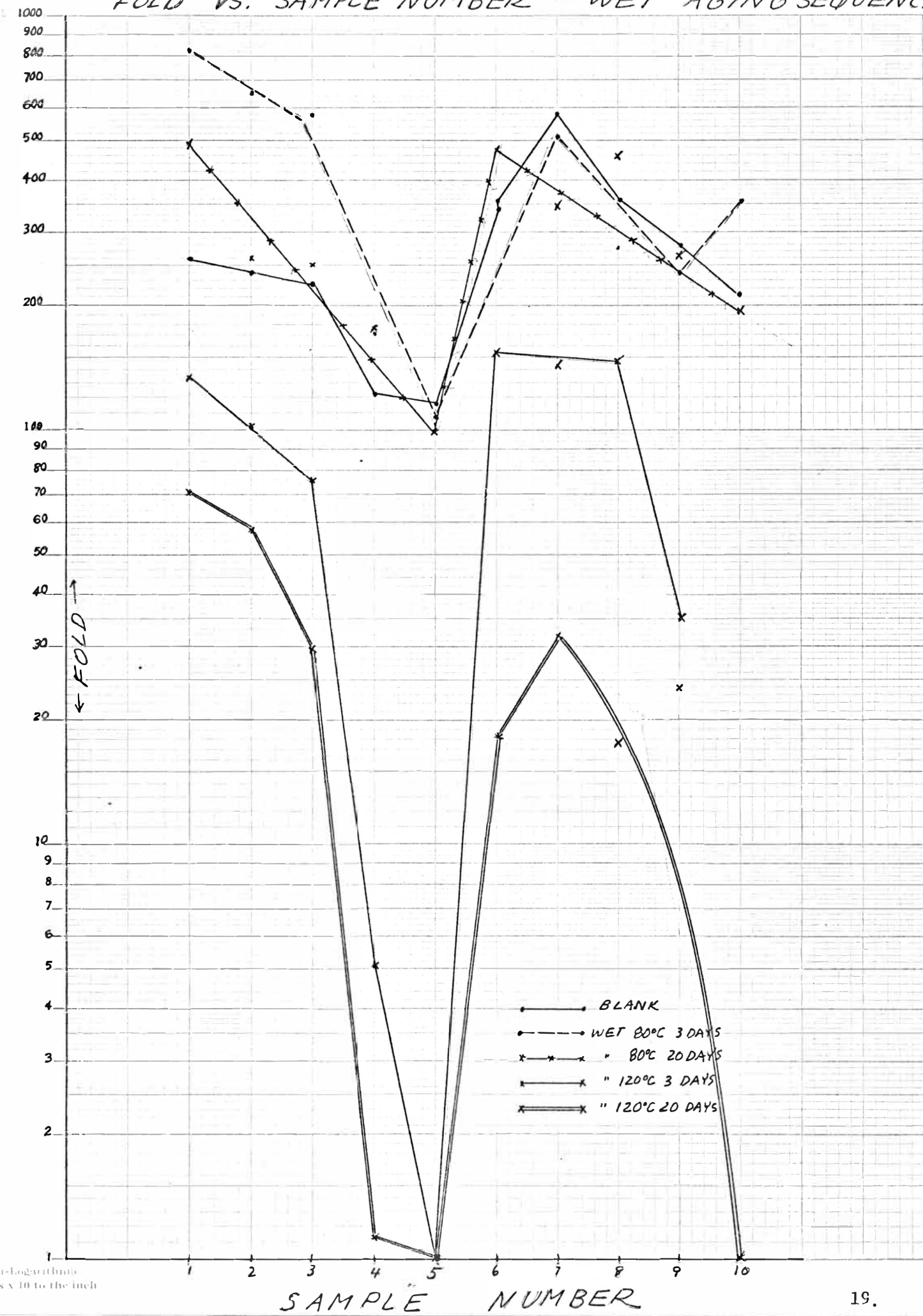
#### Tensile

The tensile strength vs. sample number graphs (see pages 21 and 22) showed the same general trends as those of folding endurance, but the lines representing the different aging cycles are more clearly separated.

Graphs of the effect of aging conditions on the tensile strength of the various samples were less helpful, but had some interesting features. In about 90% of the cases, the curves were found in the following order; Dry 80 C, Wet 80 C, Dry 120 C, Wet 120 C. General downward trends were found in 90% of Dry 120 C and Wet 120 C, but only about 50% of Dry and Wet samples at 80 C. (see pages 23-27)

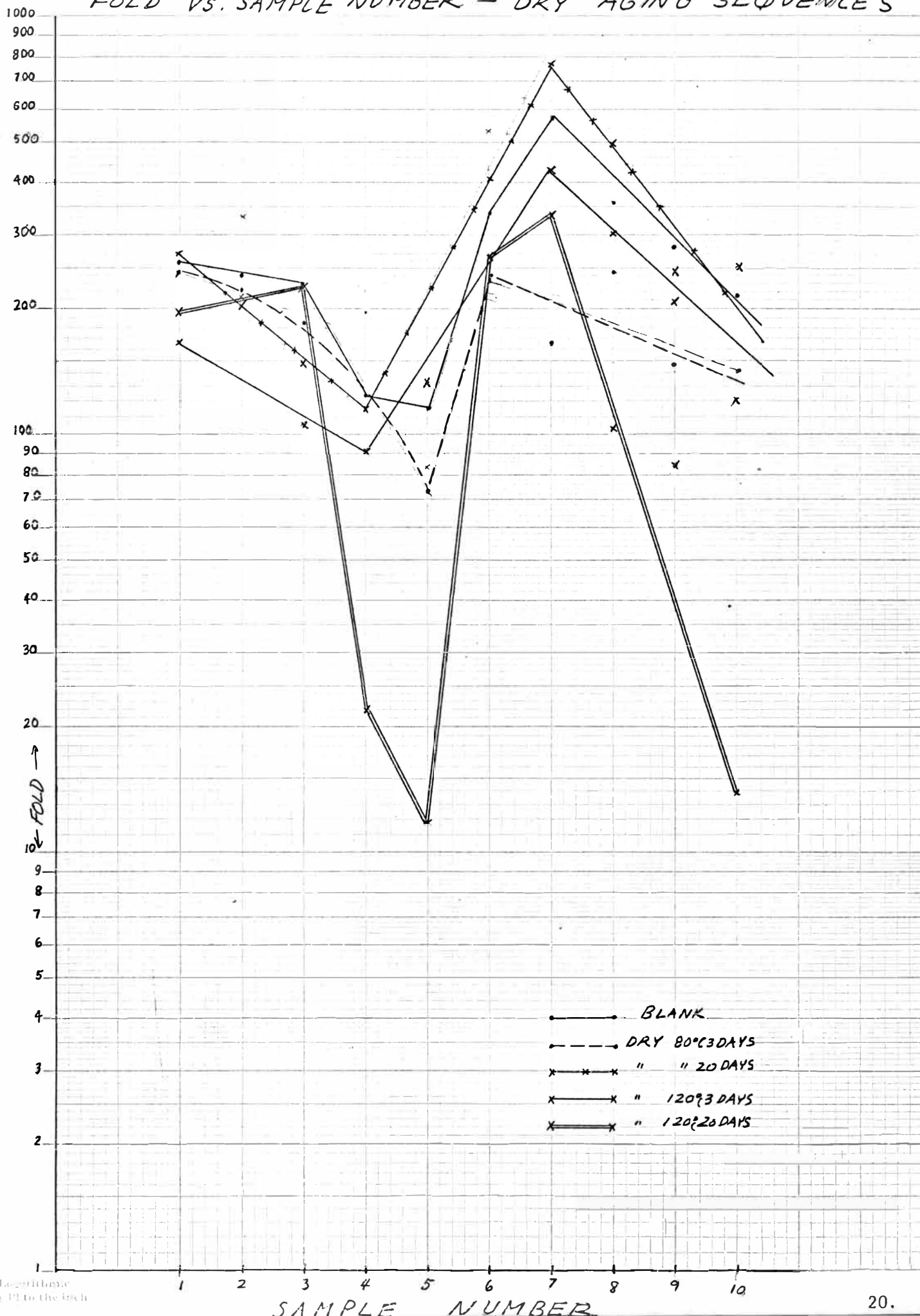
A comparison of two sets of tensile tests is seen on the chart on

# FOLD VS. SAMPLE NUMBER - WET AGING SEQUENCES

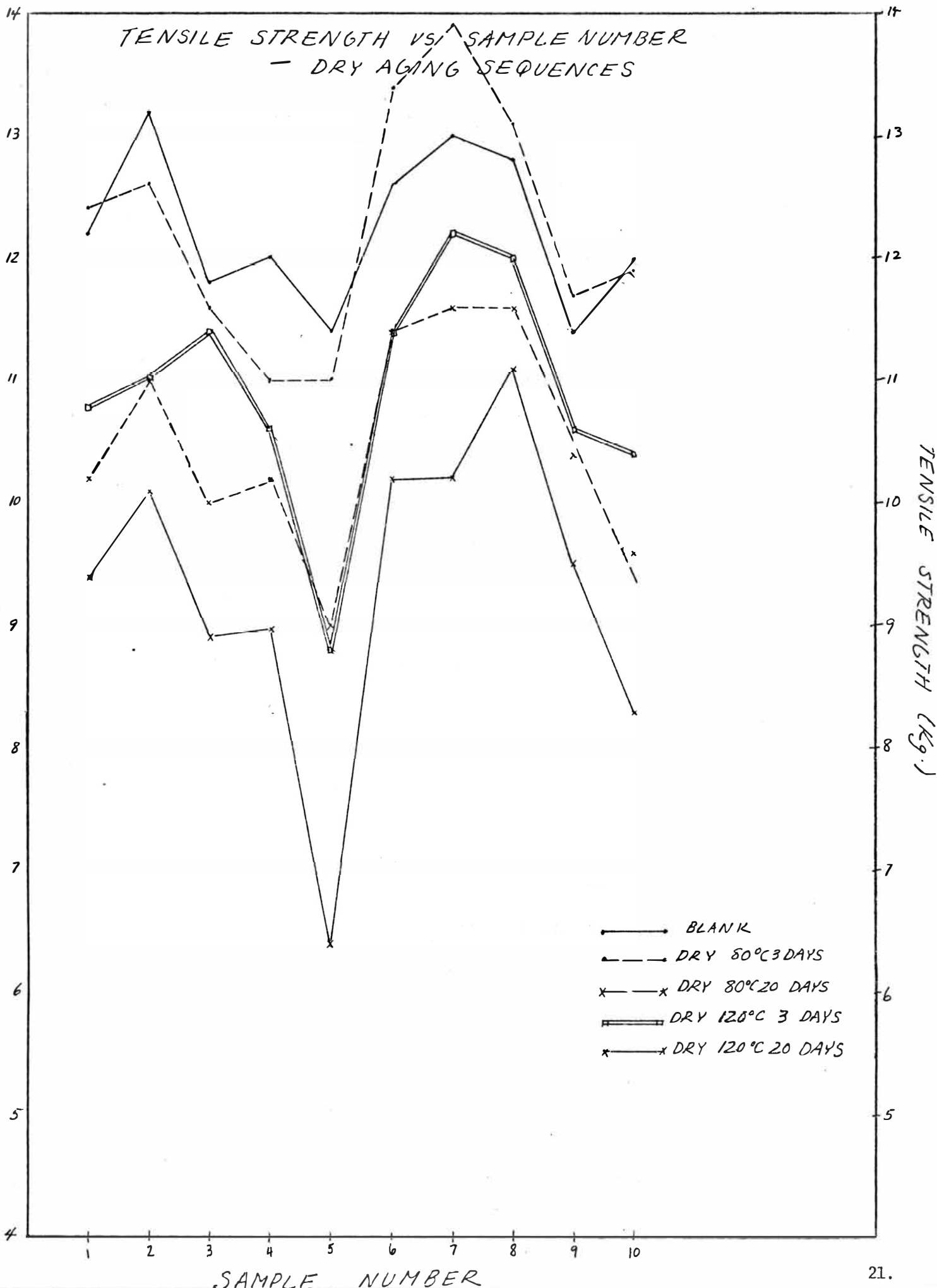




# FOLD VS. SAMPLE NUMBER - DRY AGING SEQUENCES

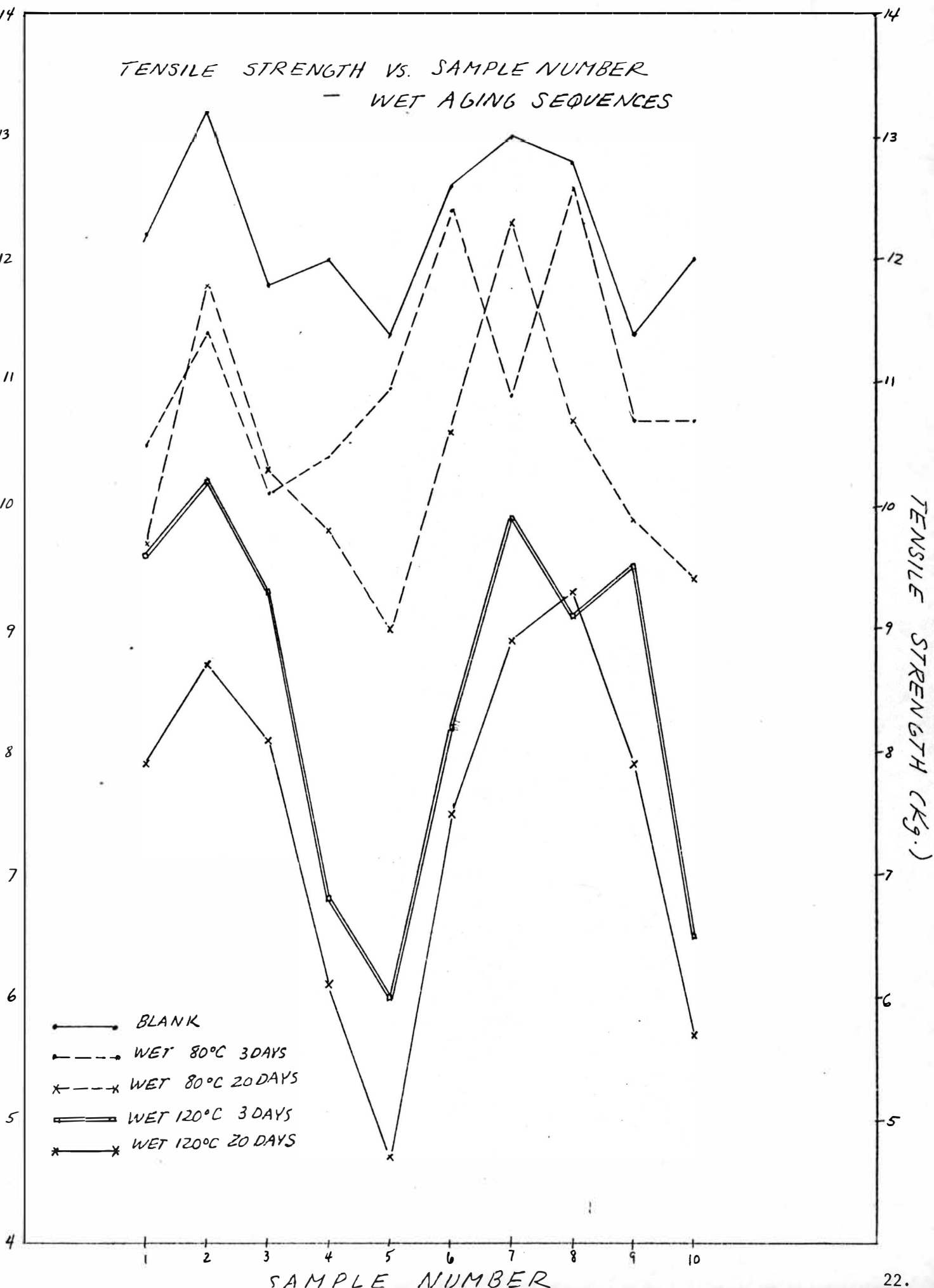


# TENSILE STRENGTH VS. SAMPLE NUMBER - DRY AGING SEQUENCES



TENSILE STRENGTH VS. SAMPLE NUMBER  
 — WET AGING SEQUENCES

- BLANK
- - -•- WET 80°C 3 DAYS
- x - - - x WET 80°C 20 DAYS
- ==•==•== WET 120°C 3 DAYS
- \* - - - \* WET 120°C 20 DAYS



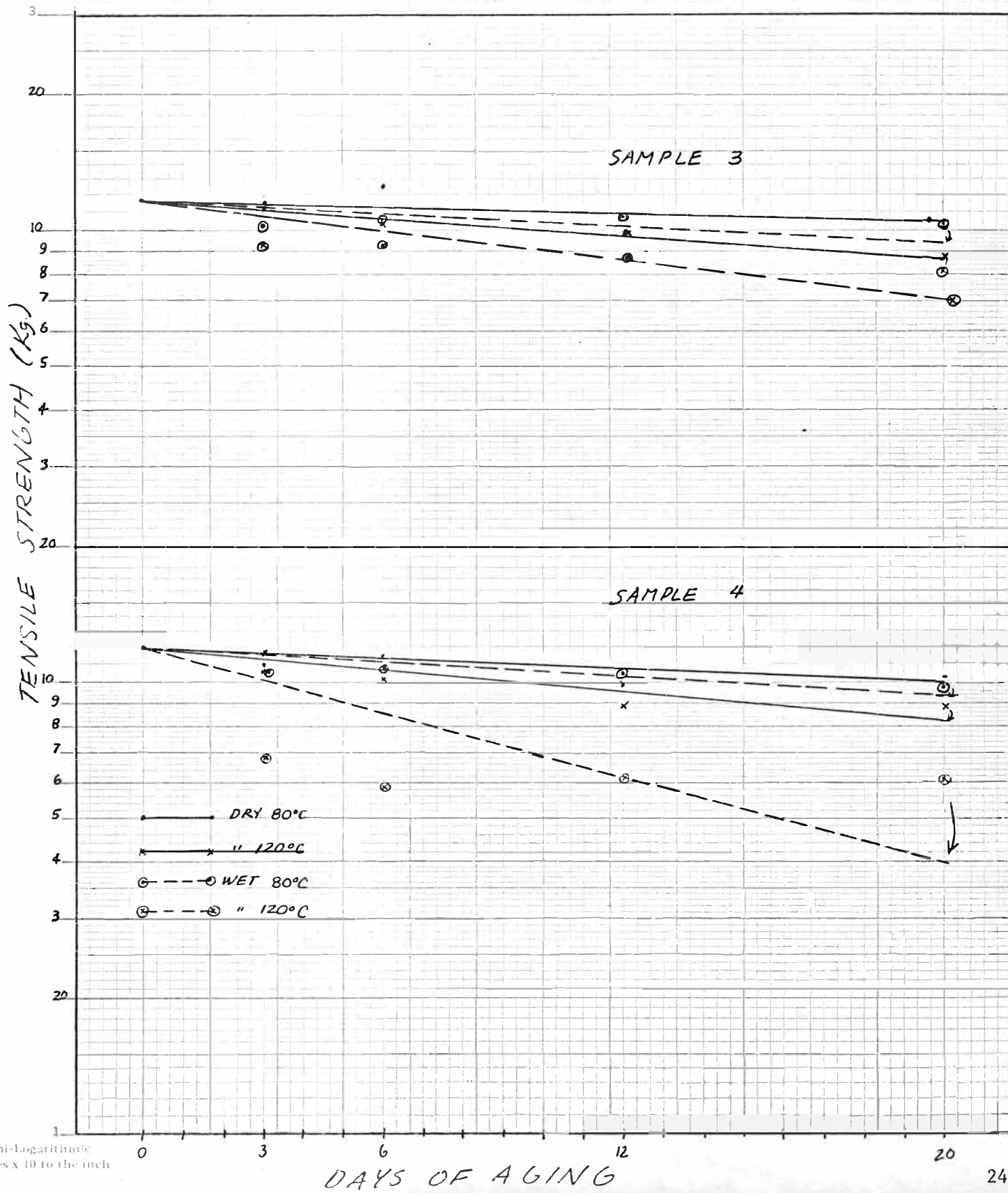
# EFFECT OF AGING CONDITIONS ON TENSILE STRENGTH

SAMPLE 1

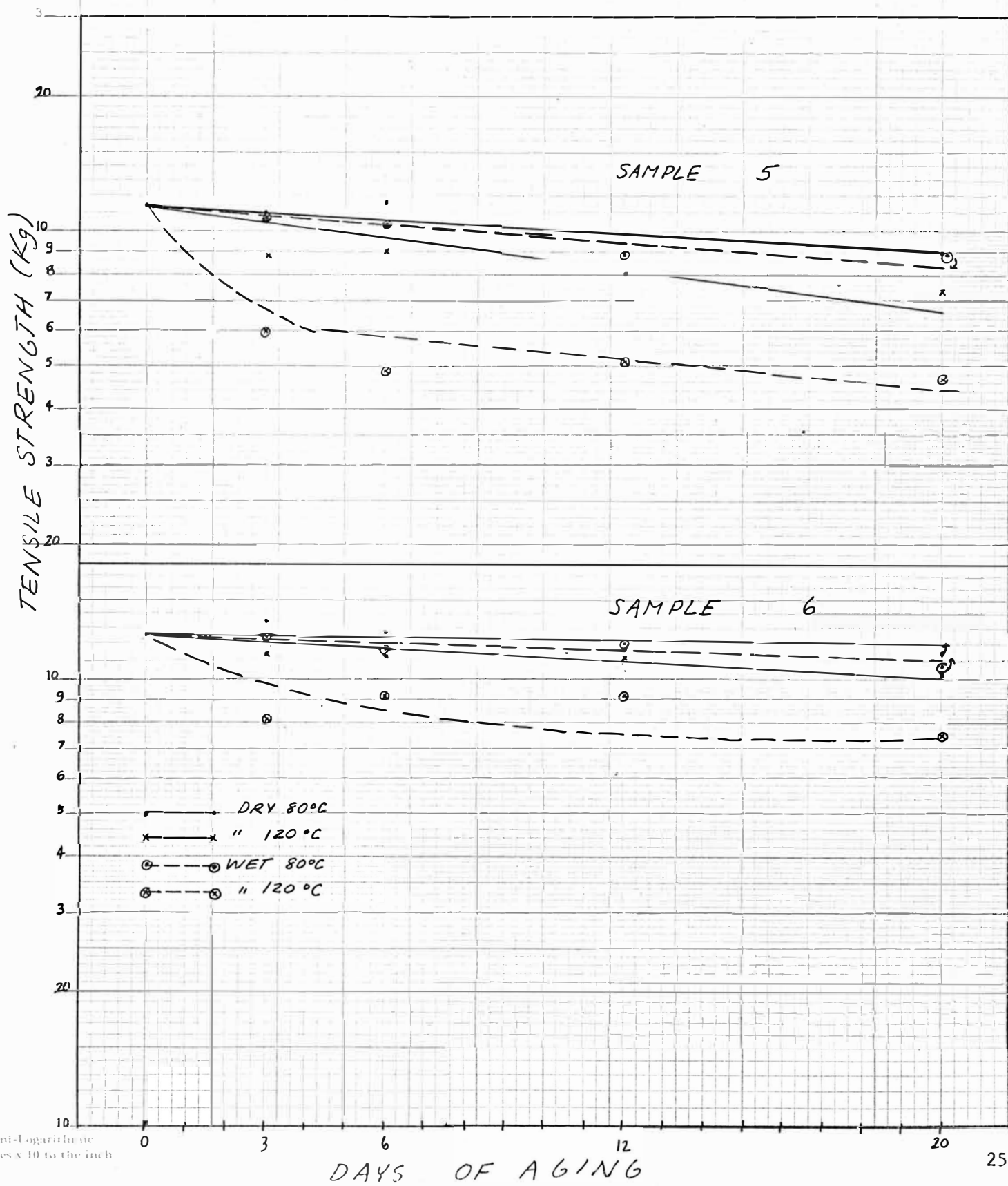
SAMPLE 2

- DRY 80°C
- x— DRY 120°C
- WET 80°C
- ⊗— WET 120°C

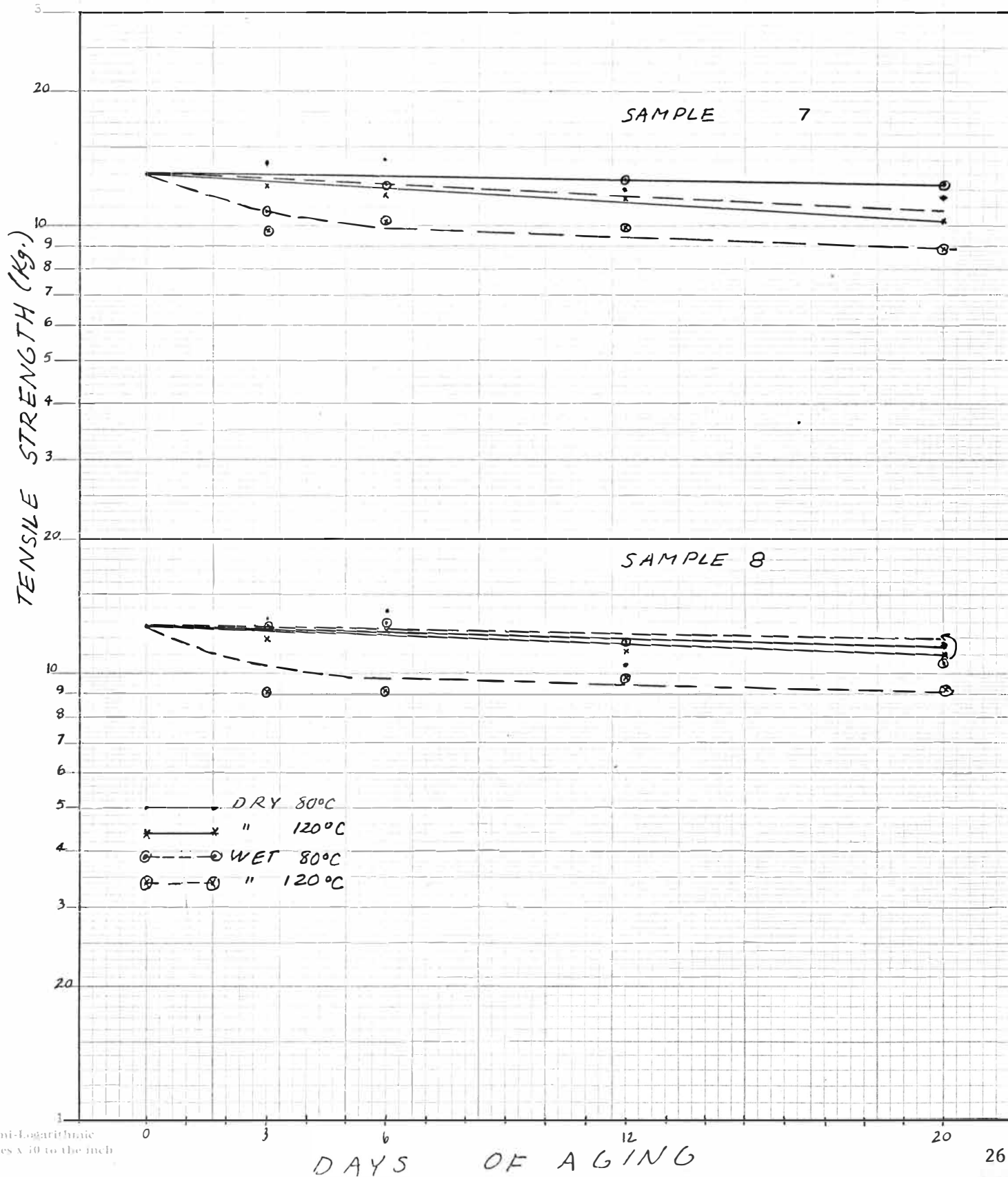
# EFFECT OF AGING CONDITIONS ON TENSILE STRENGTH



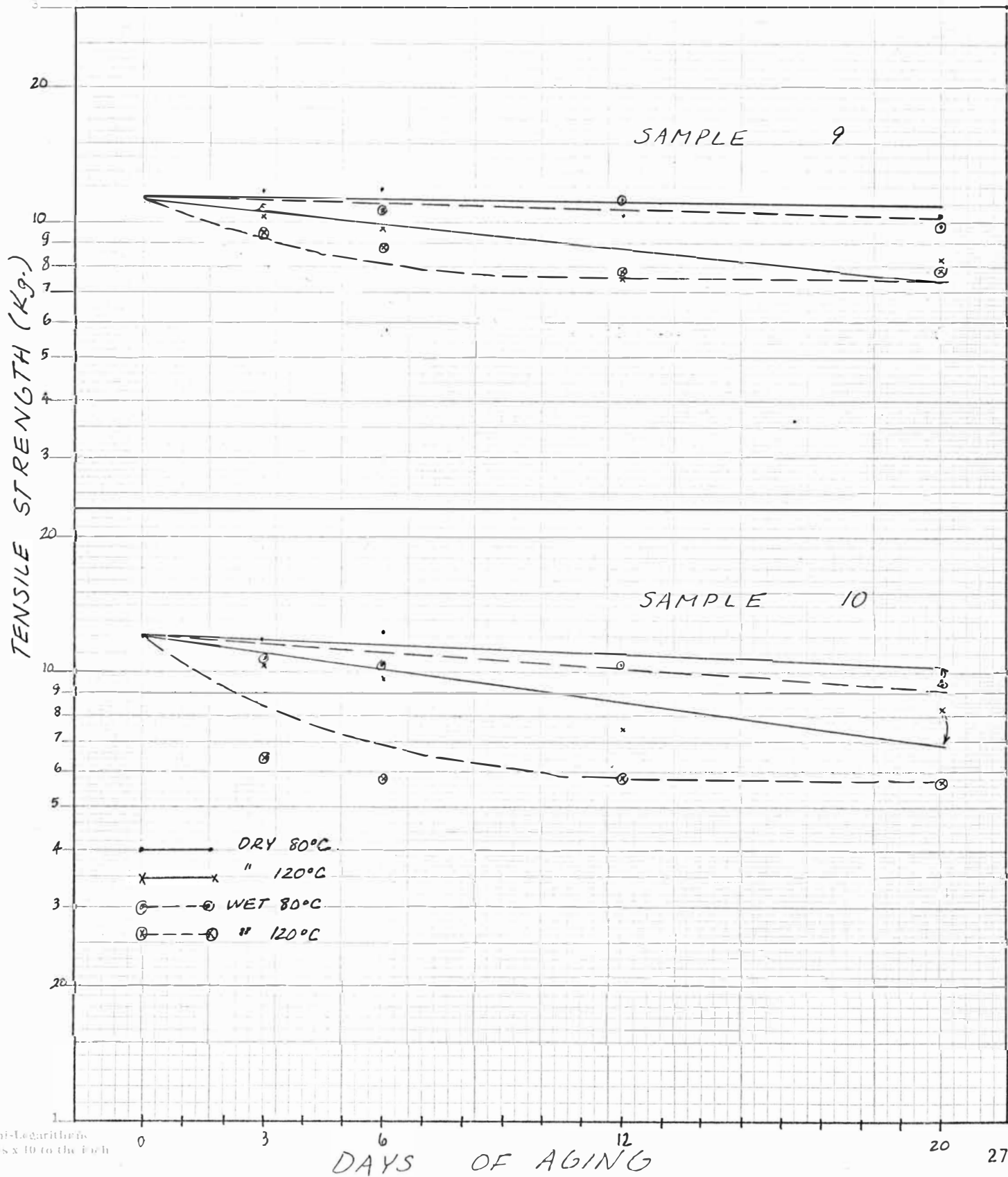
# EFFECT OF AGING CONDITIONS ON TENSILE STRENGTH



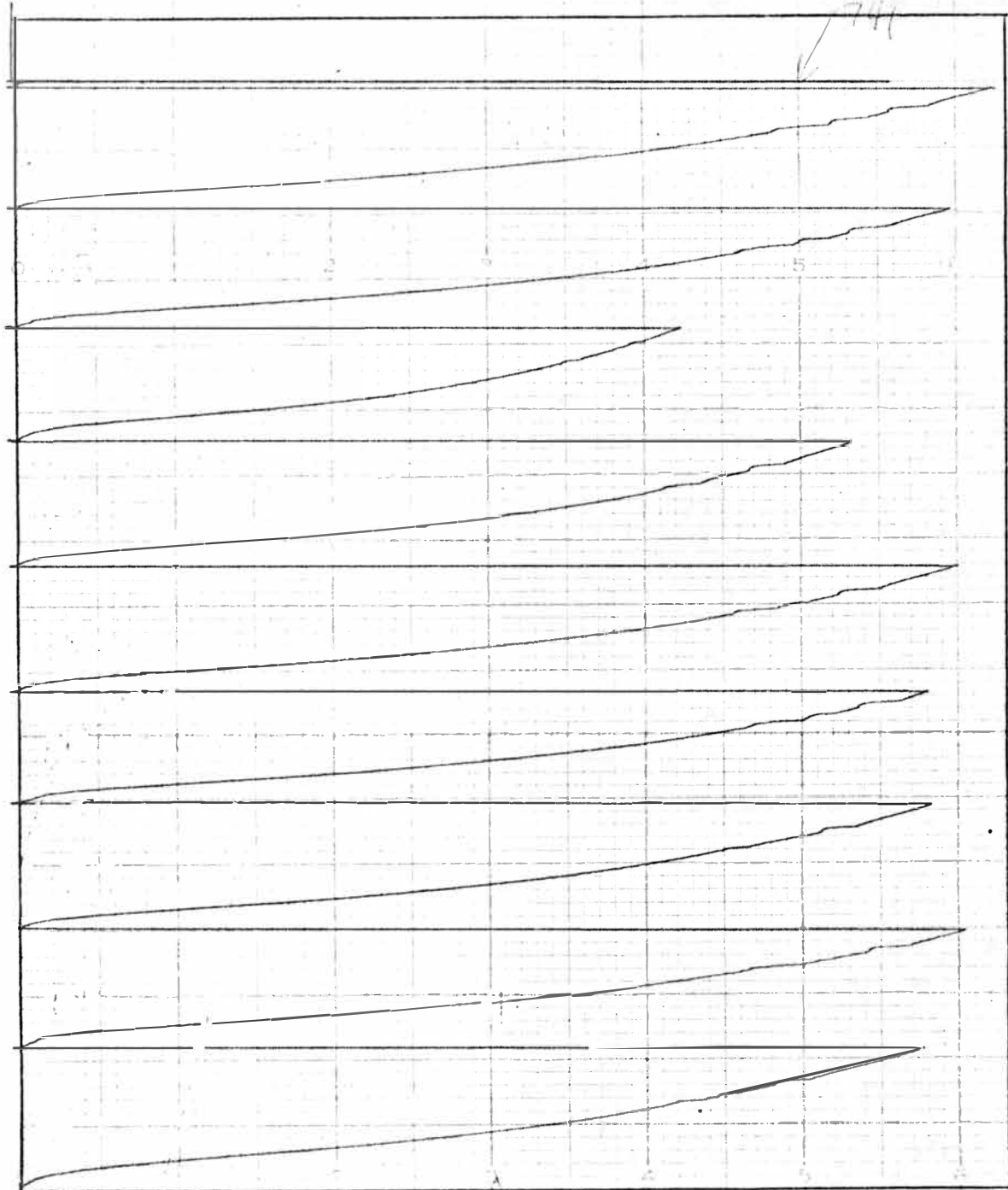
# EFFECT OF AGING CONDITIONS ON TENSILE STRENGTH



# EFFECT OF AGING CONDITIONS ON TENSILE STRENGTH

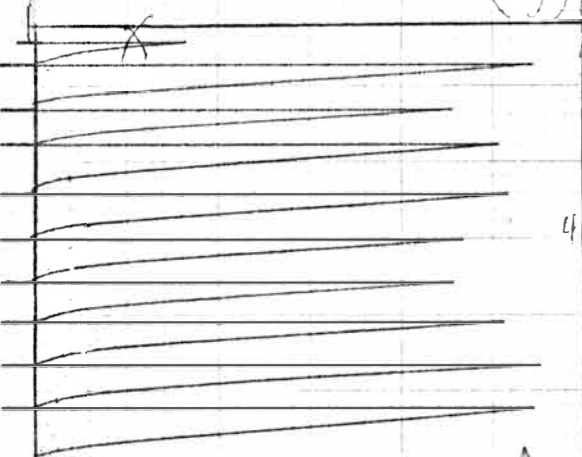






(5)

BLANK (0 HOURS) 20kg FSL



	BLANK (0 HOURS)	WET 120° (12 DAYS)
TENSILE	112 ± 12	51 ± 4
% STRETCH	1.82 ± .15%	.53 ± .10%

WET 120° 12 DAYS  
(20 kg FSL)

(5)

page 28. The unaged blank and the Wet 120 C 12 day sample were both tested at 20 kg FSL. As can be seen, not only did the tensile strength drop 55%, but the stretch decreased 71%!

Some of the more severely aged samples crumbled slightly when trimmed to remove the staples before testing.

#### pH (Indicator)

This method yielded interesting but vague data. The graph of pH (Indicator) vs. Sample number definitely has the correct shape, closely resembling the graphs of folding endurance and tensile strength.

(see pages 30 and 31)

#### pH (Möller Electrode)

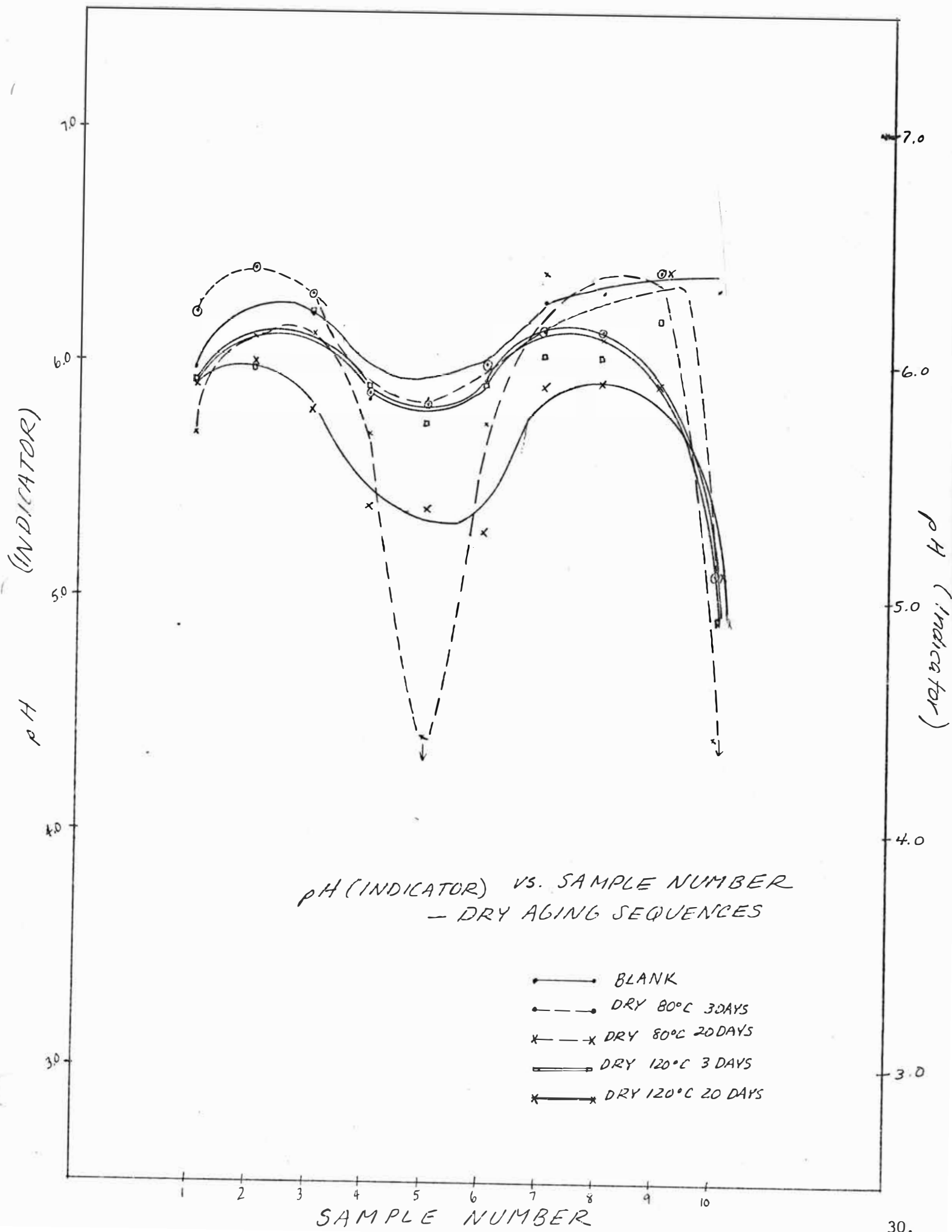
Electrometric pH was more precise than Indicator pH. The standard deviations encountered were smaller and the graphs of pH vs. Sample number had more detail. (see pages 32 and 33)

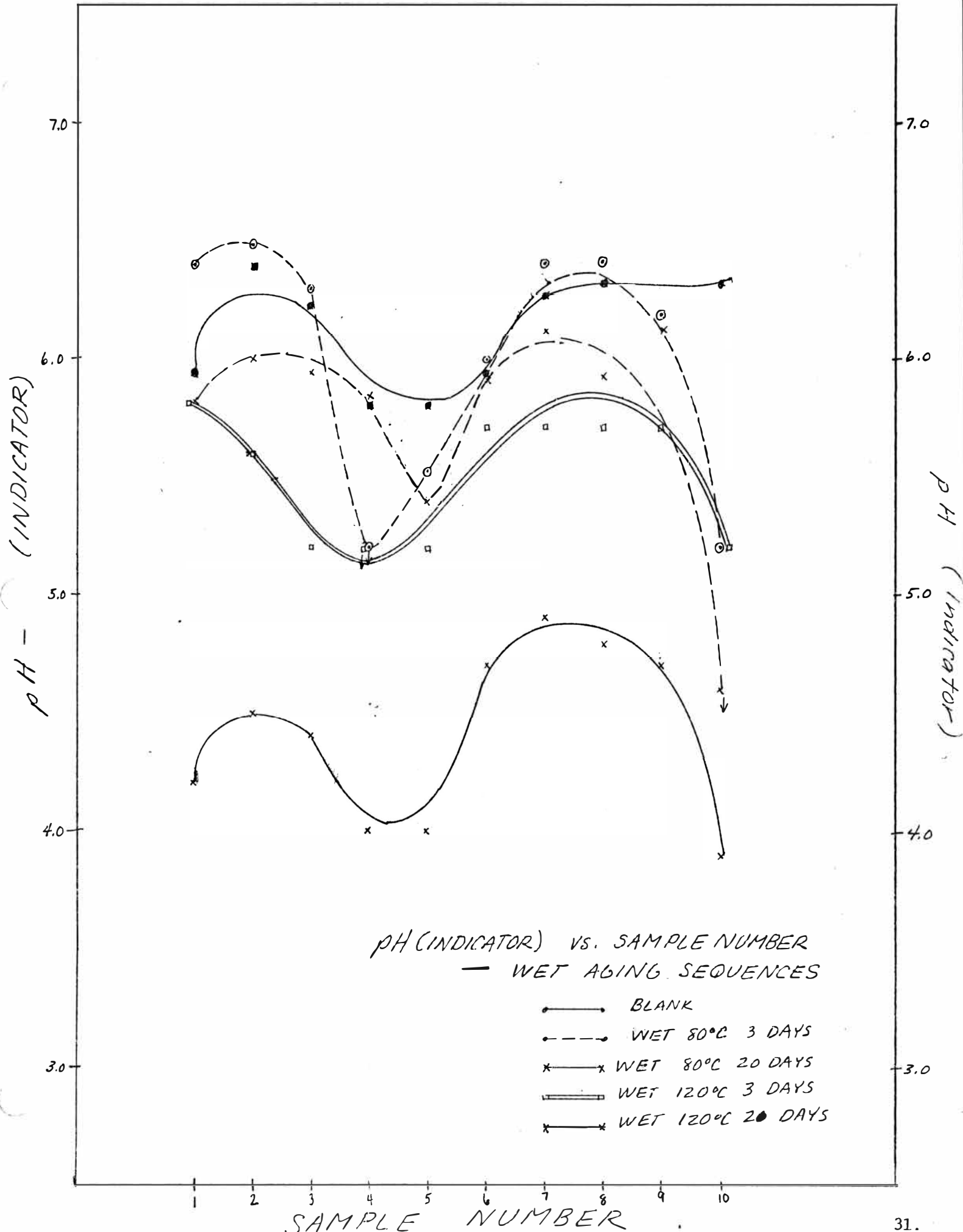
### Discussion of Results

#### General

The pilot plant humidity room did not conform to the Tappi Standard 73.4 $\pm$ 1.8 F dry bulb, 50 $\pm$  2% R.H. at any time during the testing period. The averages for one month were 66.27 $\pm$ 1.95 F dry bulb and a relative humidity of 84.2  $\pm$  8.91%. This R.H. is so high that the tests results cannot be considered to be standard.

The 10 samples made for this project were compared using the t-test. Referring to the figures on pages 34 and 35 it can be seen that most of the samples are different even in the Blank. The difference becomes even greater as the aging progresses.

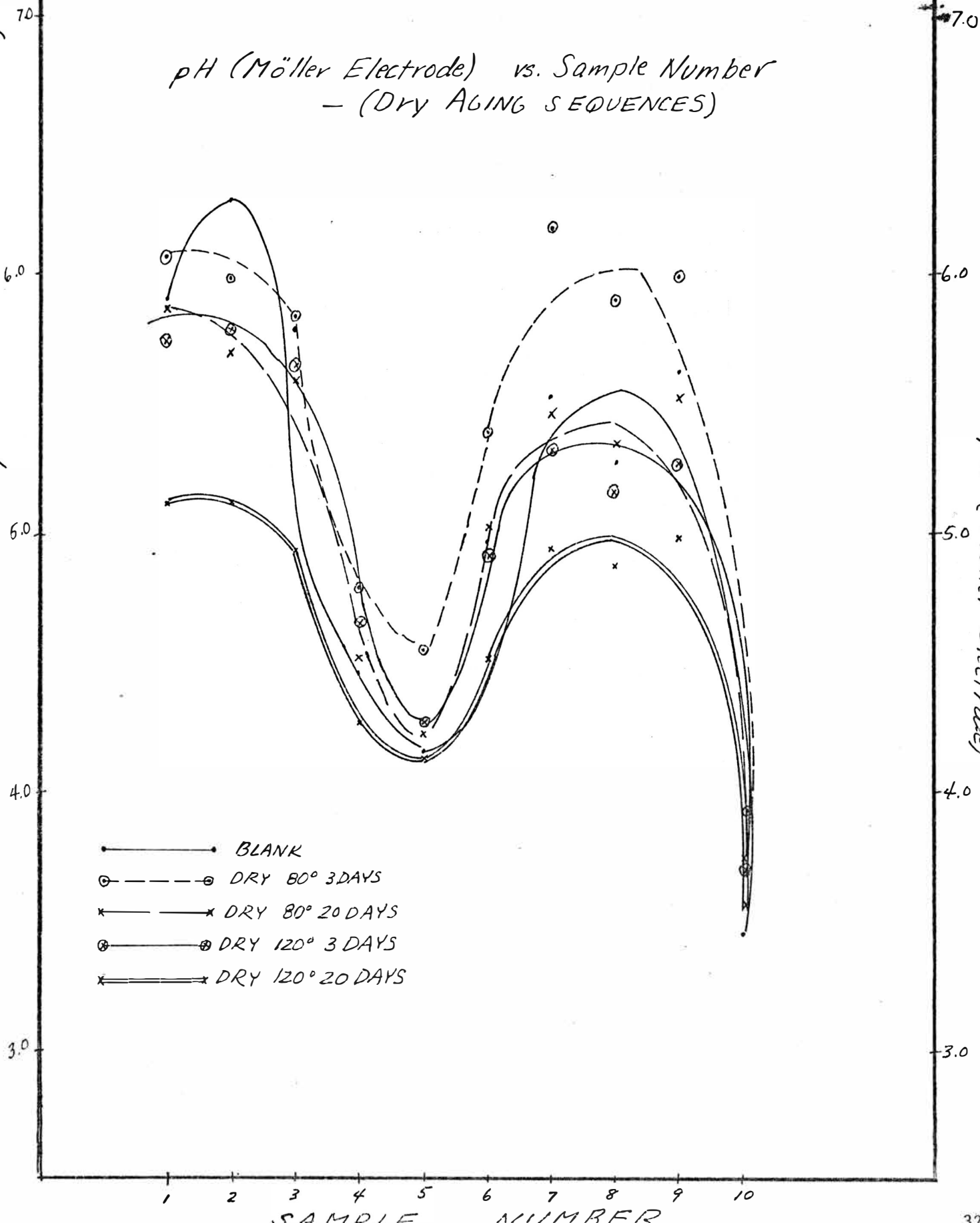




pH (Möller Electrode) vs. Sample Number  
 - (Dry Aging SEQUENCES)

pH (Möller Electrode)

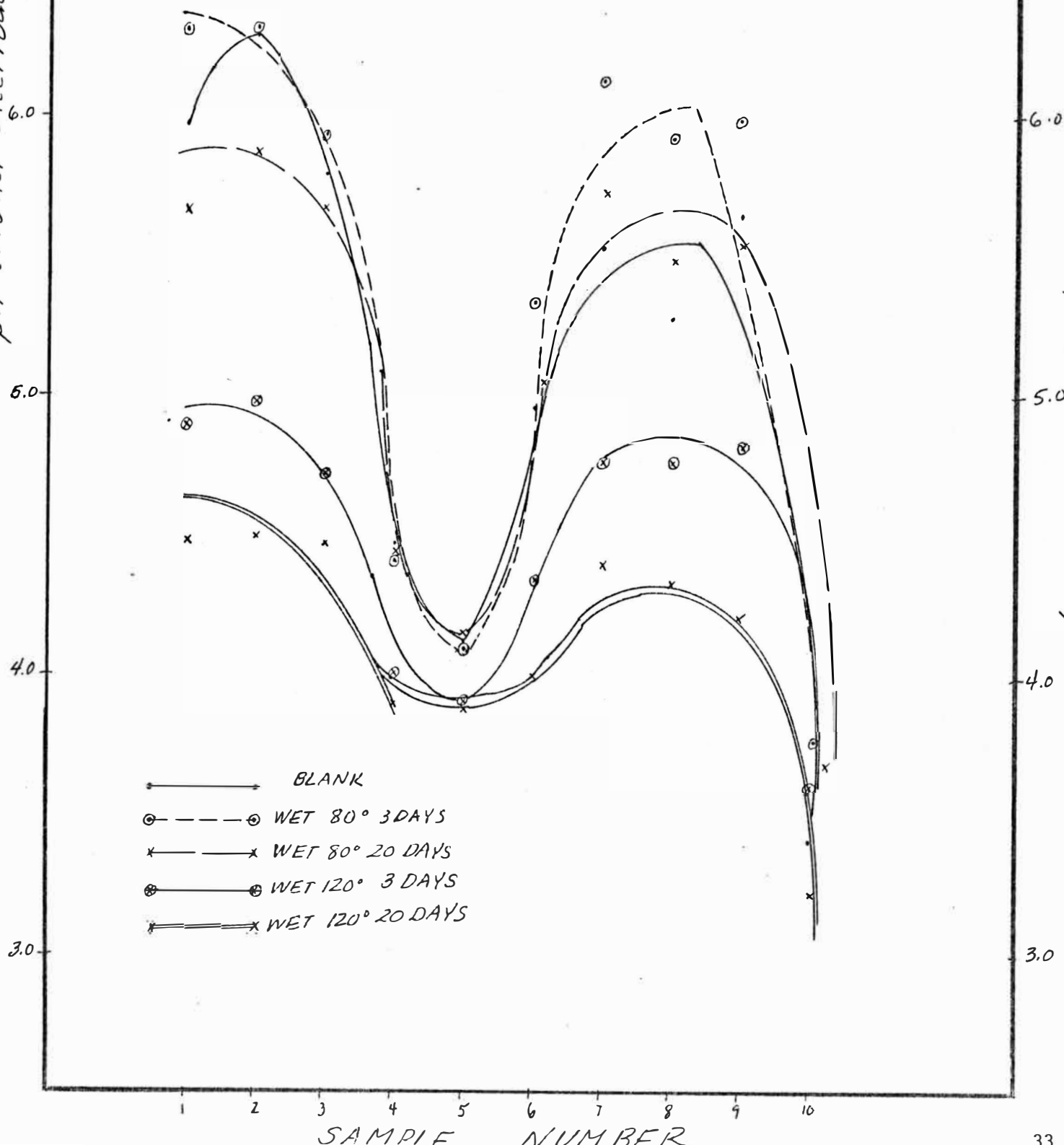
pH (Möller Electrode)



pH (Möller Electrode) vs. Sample Number  
 — (WET AGING SEQUENCES)

pH (Möller Electrode)

pH (Möller Electrode)



SAMPLE NUMBER

1 2 3 4 5 6 7 8 9 10

=	<	<			<			<	<
<	=	<						<	<
<	<	=						<	<
			=	<					
			<	=					
<					=		<	<	
						=			
					<		=	<	
<	<	<			<		<	=	<
<	<	<						<	=

t-matrix of BLANK fold

SAMPLE NUMBER

1 2 3 4 5 6 7 8 9 10

1	=	<							
2	<	=							
3			=				<		<
4				=					<
5					=				
6						=		<	
7			<				=		
8						<		=	
9			<						=
10				<					=

t-matrix of WET 120°C 20DAYFOLD

= equal by definition  
 < not necessarily different (95% certain;  $\alpha = .025$ )  
 □ different

	1	2	3	4	5	6	7	8	9	10
1	=	<								
2	<	=								
3			=						<	
4				=						
5					=					
6						=		<		
7							=			
8						<		=		
9			<						=	
10										=

COMPARISON OF  $t$ -MATRIX OF  
BLANK FOLD & WET 120°C 20 DAY FOLD

= equal by definition  
 < not necessarily different (95% certain)  
 □ different



### Folding Endurance

The value of folding endurance in evaluating the effects of artificial aging is somewhat obscured by the large standard deviations normally associated with the test. This number average standard deviation (in percent) often exceeds 30% even when the utmost care is taken to reduce sources of error in testing.(40) Graphing the test results on semi-log papers smooths out the data considerably. Two MIT fold testers were used to speed up the testing. Based on t-tests on the means and standard deviations of both fold testers when used together to get data for this project, the following trends were observed. In 68% of the comparisons, there was no apparent difference between the testers. Of the remaining 32%, 3/4 were from instances where folding endurance values were less than 200. Below this point, instrument problems and paper inconsistencies seemed to have an increasing effect on the amount of error in the test.

### Tensile Test

The reduction in tensile strength on aging was used as a basis for reducing fold load. This use implies some faith in the ability of the test to show strength changes as paper ages. As mentioned before, the strength curves for fold and tensile have the same general shapes, though the range of tensile strengths seen is much smaller. This could be a problem. The curves for tensile strength vs. sample number are clearly separated, but the inclusion of the standard deviation would render them much less useful and clear.

The large percent elongation loss on aging is an indication of the lessening flexibility of the paper. Samples with very little stretch

(like that shown in the lower portion of page 28) broke in the fold tester after only 0-20 folds.

#### pH (Indicator)

The choice of indicators for this test was based on the work of several paper restorers. (35,36,43) The researchers were apparently more interested in identifying pH limits than in identifying actual, precise pH values. As mentioned before, restorative treatment is indicated when the pH of a book or artwork on paper dips below a critical point (usually around pH 5). This would explain why pH's below about 5.5 were difficult to pin down with the 6 indicators chosen. Past this point the restorer would not really be interested in how bad the situation was, since treatment would be indicated anyway.

Distinguishing between color variations produced by the indicators was complicated by a number of factors.

Especially in the case of the wet aged papers, considerable discoloration of the paper samples occurred on aging. This yellowing interfered with the interpretation of the colors, causing a problem, since so many color variations are possible just on a white substrate.

Personal judgement becomes an important variable when colors must be compared, particularly when no standard is available and the indicator shades change subtly with time as they dry.

#### pH (Müller Electrode)

This electrode was chosen on the recommendation of A. King (36,43,47) and W.E. Falconer (36,43,48). It was well adapted to measuring the pH of paper as it is easy to handle (being a slender combination electrode) and

only a very small surface area must contact the paper for it to work. King uses such an electrode in her work as a paper restorer at the Museum of Modern Art in New York.

The resolution between samples was much greater than that seen when using the indicator solutions, and the standard deviation of the test was very small. Accuracy appeared to be maintained across the whole range of pH values encountered. Human errors eliminated by the Beckman pH meter, the results just had to be better.

#### Wet and Dry Aging

The t-test was used to compare wet and dry aging at the same temperature for the same time periods.

At 80 C 50% of the point pairs were not necessarily different. At 120 C only 10% were not different.

The wet aging, particularly at 120 C caused larger losses in strength properties than did the dry aging at corresponding temperatures. This seems to confirm the fact that dry aging is not a true indication of natural aging since it is not as hard on the paper.

#### Conclusions

A certain amount of the error due to the fold data was caused by the almost constant technical difficulties experienced by the MIT fold testers. The following problems were encountered:

1. miscounting
2. impossible to zero accurately
3. spontaneous sample breaking due to tester malfunction (parts were getting bound up in the tester).

As pointed out in the literature, (40) folding endurance is dependent upon the temperature and humidity conditions in the testing chamber. While the high, fluctuating R.H. in the testing lab was not necessarily the source of all the error, it did at least render all of the data non-standard.

An adapted range of indicator solutions could be used to check the pH of paper. The selection used here was sufficient for accurate pH determination only above pH 5.5.

The Möller pH electrode has interesting possibilities for the determination of surface pH as it is small, quick-reading and precise. It does not require a large wetted area, either.

#### Recommendations

The work seemed worthwhile enough for it to be verified and expanded under standard conditions. Sufficient sample still remains to continue the experiment.

Further dry and wet aging cycles at different temperatures would give the data points needed for kinetic analysis of the data. 100 C would be the next logical choice for a temperature. A comparison of the kinetic analysis of the dry and wet aged samples could follow.

Possibilities for more sensitive results, especially below pH 5 are as follows.

Indicator	Color Change	pH Range
N-N-dimethyl-p(m-tolylazo)aniline	red-yellow	2.5-4.8
Congo Red	blue-red	3-5
Methyl Orange	red-yellow	3.2-4.4
Ethyl Orange	red-yellow	3.5-4.8

Resazurin	orange-violet	3.8-6.5
Lacmoid	red-blue	4.4-6.2
Alizarin Red	yellow-red	4.6-6

Especially if a pH meter was not available, further investigation into indicator use for the determination of the surface pH of paper would at least be useful.

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Comparison of Blank, Dry 120 C 20 days and Wet 120 C 20 days

